# FLORIDA SOLAR ENERGY CENTER

*Creating Energy Independence Since 1975*

# NASA Hydrogen Research at Florida Universities

**Dr. David L. Block**

**2006 International Workshop on Pollution Prevention and Sustainable Development**
**November 1-2, 2006**
**Colorado Springs, Colorado**

A Research Institute of the University of Central Florida

# Florida Solar Energy Center

*Creating Energy Independence Since 1975*

- Hydrogen Program at FSEC
- NASA Program Technology Areas/ Highlights
- Key Project Results
  - H2 Production
  - H2 Storage – AB Catalysts
  - Sensing – Smart Pigments
  - H2 Separation
  - Fuel Cells

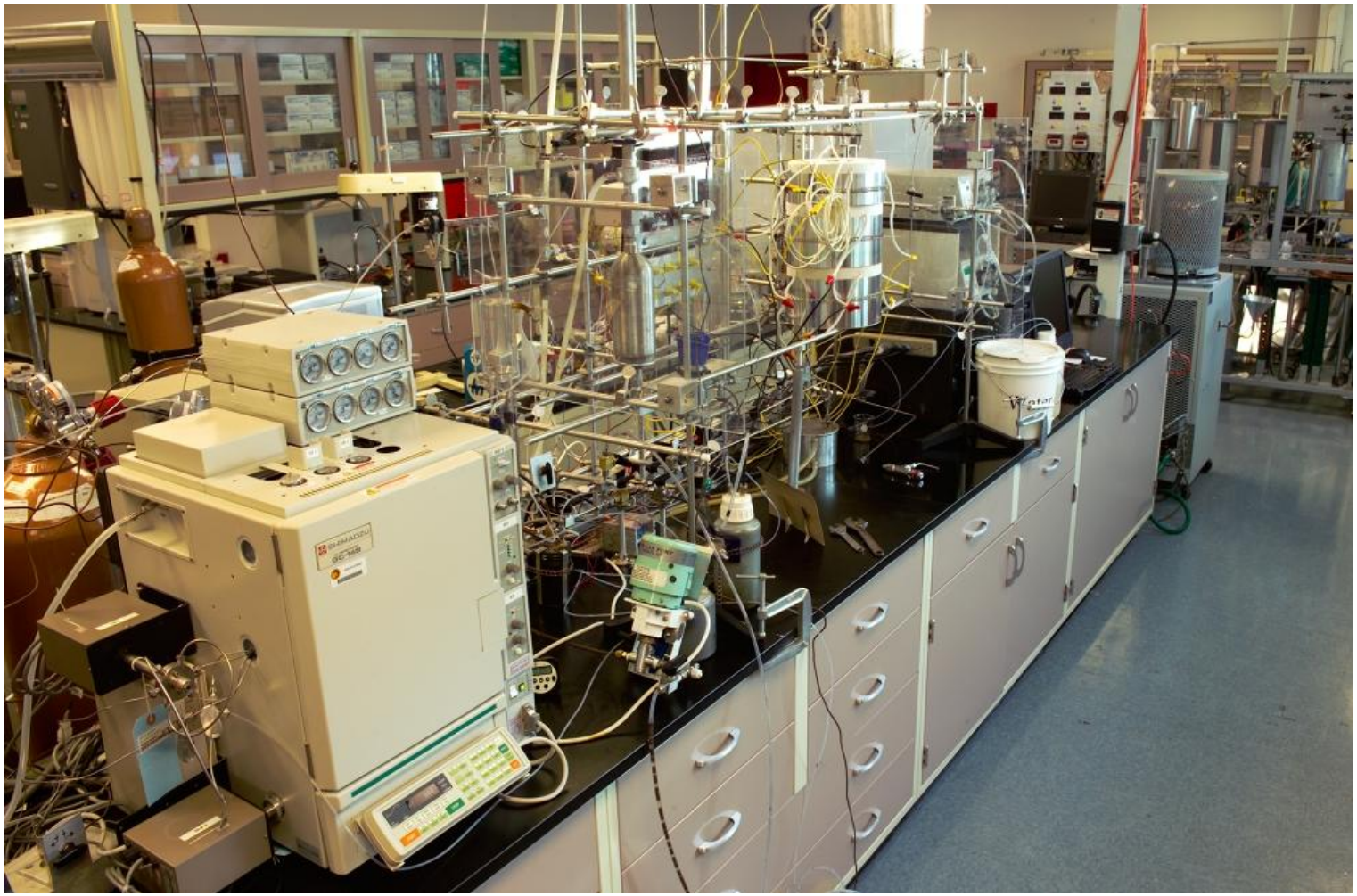
# FSEC Hydrogen R&D Division

## Goal:

*"Make hydrogen a key component of a clean & secure energy future."*

# $H_2$ Labs

# $H_2$ Labs (cont'd)



# $H_2$ Labs (cont'd)

# FSEC $H_2$ R&D Highlights

- Hydrogen research began in 1983
- Externally funded R&D > $35 million
- Primary funding from DOE & NASA
- Strong chemistry & ChE faculty
- Patents:27 issued & 5 pending
- Over $1.5 million in laboratory equipment and facilities.

# NASA Hydrogen Research Program

- In fourth year
- Total program funded at $28 million
- FSEC manages all activities external to UF
- Funding thru NASA Glenn Research Center

# Participating Universities

- University of Central Florida
- Florida State University
- University of South Florida
- Florida International University
- University of West Florida
- Florida A&M University
- University of Florida.

# NASA Grant Highlights

## FSEC managed Projects

- Individual university projects: 42
- Faculty/staff involved: close to 90
- Students involved: > 100
- Publications: > 120
- Presentations: > 120
- Patent applications filed: 20

# Technology/Universities

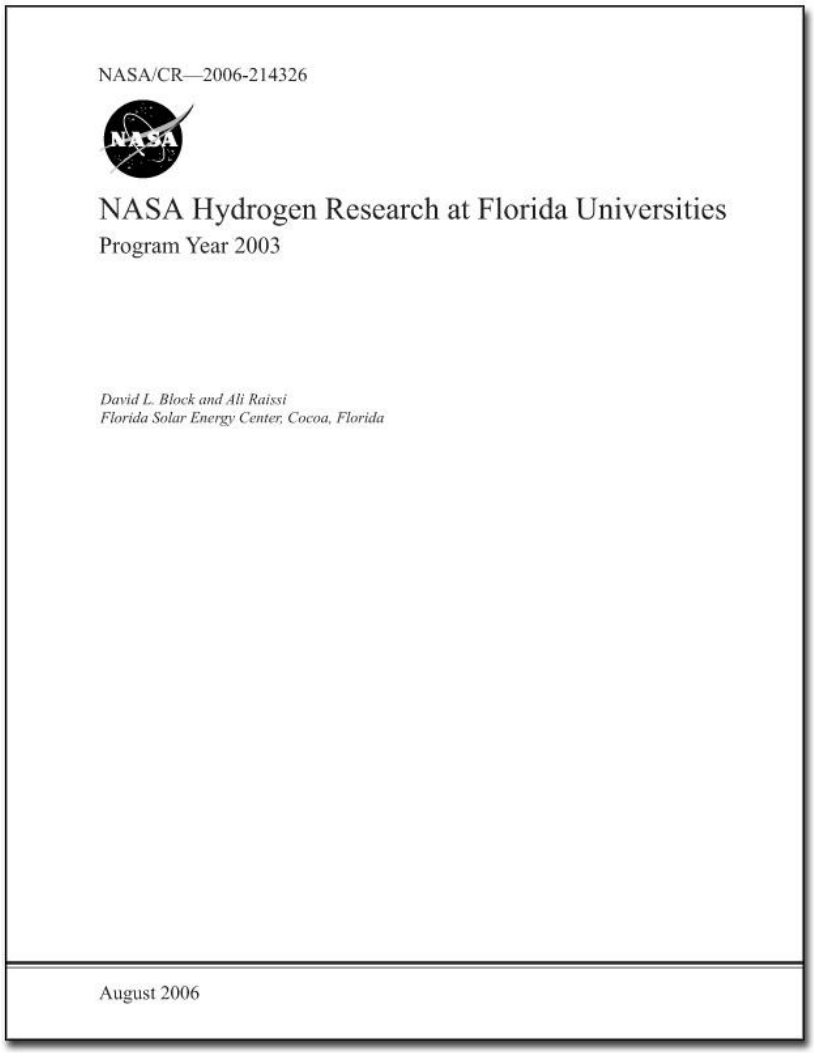
| | |
|---|---|
| Hydrogen Production R&D | FIU, FSEC, USF, UF |
| Densified Hydrogen & Cryogenics | FSEC, FSU, UF |
| Sensors & Detectors | FSEC, UCF, USF, UF |
| Storage R&D | FSEC, USF, UF |
| Separation & Purification | FSEC, UCF |
| Resource Assessment & Software | FIU, UWF |
| Fuel Cells Research | FSEC, UF, FAMU |
| Education & Outreach | ALL Universities |

# *Importance to NASA*

**Potential savings for NASA operations**

- Storage tank losses -- $250 k/year
- Local production -- $4.7 M/year
- New sensor technologies -- $500 k/year
- Densified propellants -- $10-20 M/launch

# NASA/CR-2006-214326



NASA/CR—2006-214326

NASA Hydrogen Research at Florida Universities

Program Year 2003

*David L. Block and Ali Raissi*
*Florida Solar Energy Center, Cocoa, Florida*

August 2006

http://gltrs.grc.nasa.gov/reports/2006/CR-2006-214326.pdf

# Projects

- Production
- Storage
- Sensors
- Fuel Cells

# Hydrogen Production

- Hydrogen sulfide methane reformation
- Catalytic reformation of fossil & renewable feedstocks
- Catalytic reformation of used lubricating oils
- Photocatalytic water splitting by dual bed dye sensitized process
- PEC water splitting by a multiple bandgap thin-film PV cell

- Solar thermochemical S-$NH_3$ water splitting cycle.

# Hydrogen Storage

- ZBO Liquid hydrogen storage
- Hydrogen purification & storage using $LiBH_4$
- Hydrogen storage in AB complexes
- LH2 tank losses.

# *Amine Borane Complexes*

- The goal is to develop amine borane based energy storage devices that generate PEMFC-grade hydrogen at low temps & without production of undesirable impurities in the gas – *e.g.* borazine, diborane, $NH_3$, etc.

# *Sensors and Detectors*

- The goal is to develop highly sensitive, fast & inexpensive $H_2$ sensors & detectors capable of operation in air or pure hydrogen environment.
  - Chemochromic
  - Nano-MEMS
  - SAW
  - Wireless

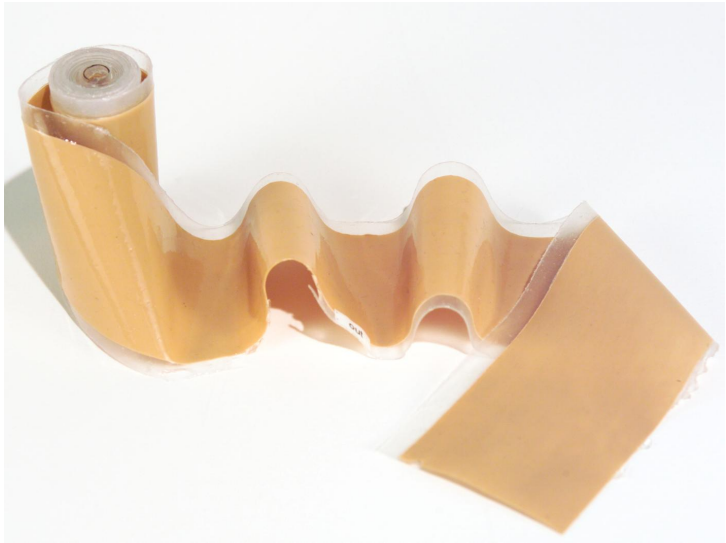
# Chemochromic Detectors

## Applications

- Hydrogen economy -

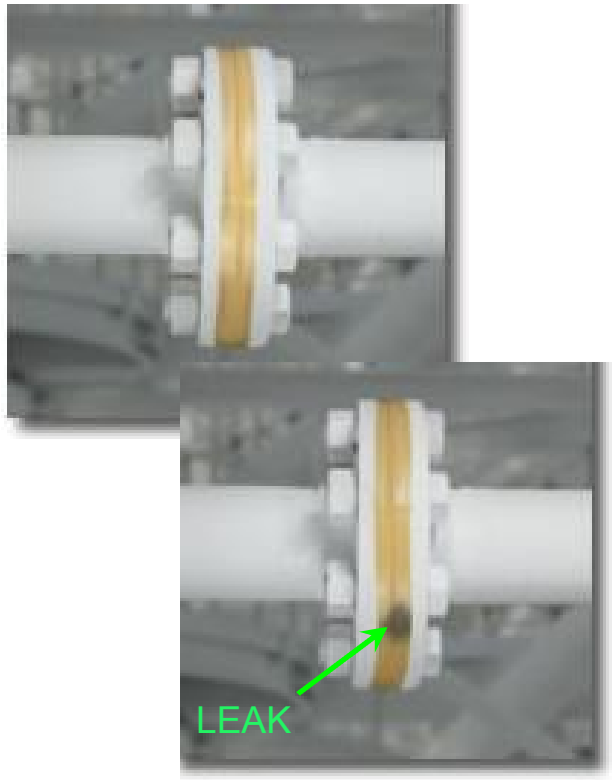
transportation, storage, vehicular fuel cells

- Refineries
- Aerospace
- Space exploration
- Semiconductor industries
- Ammonia plants
- Hydrogen liquefaction plants
- SMR plants
- Hydrogenation of foodstuff

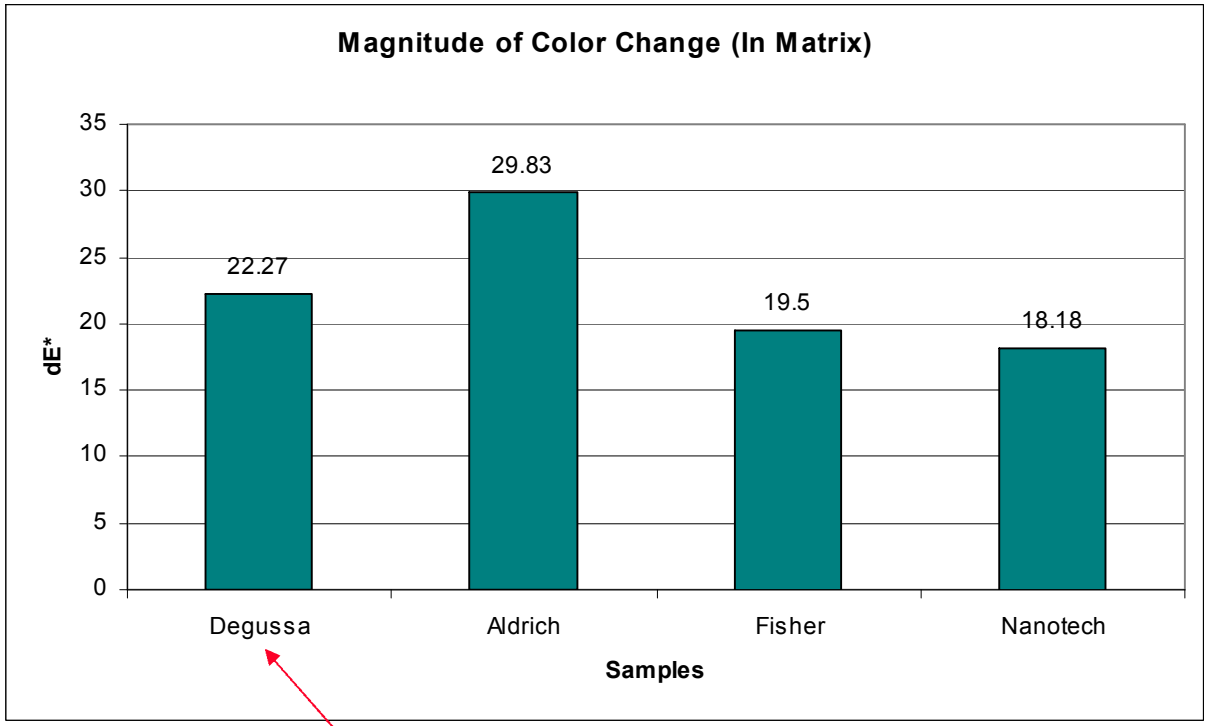


# One-time Use Sensors

- Utilize PdO based pigments
- Change color at temperatures as low as -40°C
- Employ gas permeable matrices for the pigment encapsulation that makes them selective toward $H_2$ detection
- Have been fielded at NASA-KSC
- Kits have been sent to other NASA Centers for evaluation.



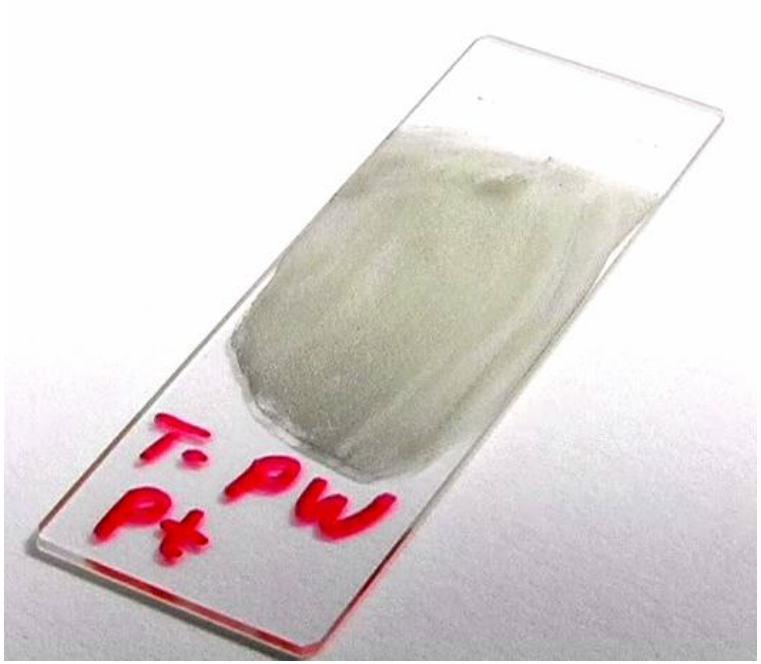
# Performance Data




*Fastest color change*

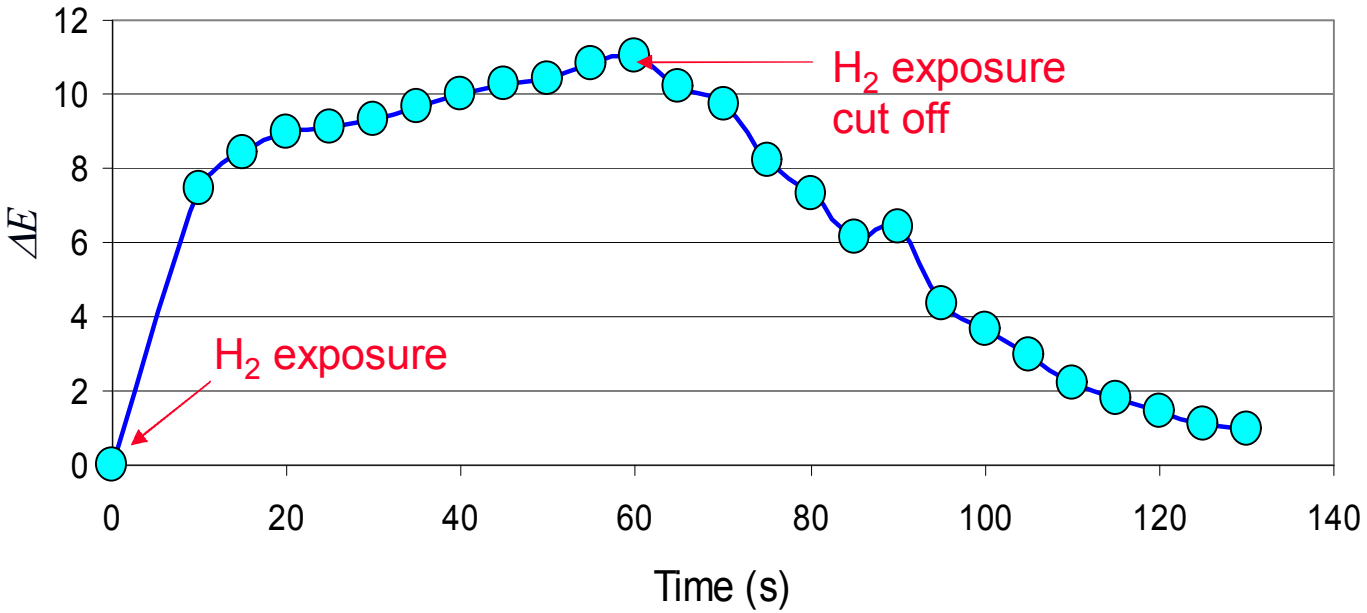
# Repeated Use Sensors

- These formulations are based on tungsten & molybdenum polyoxometales for “repeated use” applications.



# Performance Data

## *Kinetics of Coloration and Bleaching of Reversible Hydrogen Detector*



# Materials Costs

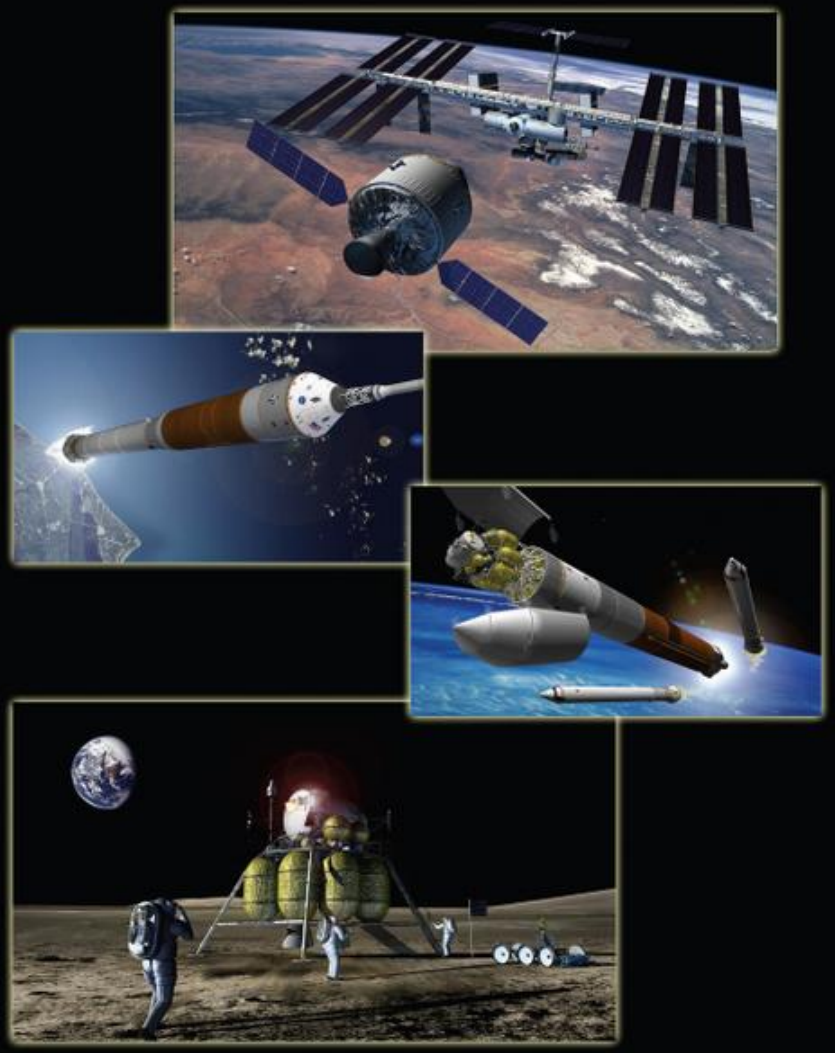
*1" Wide Chemochromic Tape*

| | Reagents & Chemicals ($/Yd) | Matrix ($/Yd) | Total ($/Yd) |
|---|---|---|---|
| One Time-Use | 0.05 | 0.87 | 0.92 |
| Repeated-Use | 0.20 | 0.26 | 0.46 |

National Aeronautics and Space Administration

**John F. Kennedy Space Center**

# 2005 Annual Report



technology development and application

## Chemochromic Hydrogen Detection

*Hazardous-Leak Detection and Isolation*

Hydrogen, a primary energy source for space exploration missions, is a main component in Space Shuttle rocket propellant. A dependable sensor is critical for hydrogen leak detection at the Shuttle launch pad, storage facilities, and other usage sites because of low explosive limits.

The Florida Solar Energy Center (FSEC), a division of the University of Central Florida, has developed a chemochromic hydrogen detection film with an irreversible response to hydrogen. This is a durable, functional material that changes color from beige to gray in the presence of hydrogen. This tape is designed to detect leaks in connection ports where hydrogen is transferred or used. It can be applied as an area monitor or integrated with personal protective equipment as an additional safeguard.

A flexible tape serves as a sensor with a platinum metal group oxide (titanium dioxide [$TiO_2$]) pigment produced according to the FSEC provisional patent application titled "Gas Permeable Chemochromic Composition of Hydrogen Sensing." Formulations were compared to find the most effective pigment. Several $TiO_2$ substrates were investigated with regard to their catalytic role. This affects the response time to hydrogen and overall color change.

Each pigment formulation was exposed to hydrogen in a glass chamber and analyzed at specific intervals. Samples were analyzed with a colorimeter to obtain the ΔE value for analytical analysis of overall color change. Samples are shown in Figures 1 and 2. The original color and final color change can be adjusted with the different formulations.

Degussa $TiO_2$ pigment responds within 15 seconds to hydrogen exposure but is less stable with time. Aldrich and Fisher $TiO_2$ formulations respond intensely to hydrogen. DuPont R103 has a unique alumina surface treatment intended to prevent discoloration that adversely affects the color change of the tape.

One of the objectives was to optimize the elasticity and ruggedness of the chemochromic tape without sacrificing the sensitivity and integrity of the film. Environmental testing was required to examine the effect of the harsh outdoor conditions in which this tape will be used. The conditions were designed to mimic application of the tape onto the KSC's cross-country hydrogen lines (Figures 3 through 5). Samples were placed at KSC's Corrosion Technology Testbed for exposure to temperature and sunlight cycling, sea spray, and rain (Figure 6). After 1 week of beachsite exposure, the samples responded faster to hydrogen than samples stored in a more controlled laboratory environment. To date, the laboratory studies include submersion in water and salt water, and exposure to an inert nitrogen atmosphere, 95 °F heat, and ultraviolet light.

These factors influence the rate of a positive color change. Continuing investigations are under way to fully elucidate the environmental effects on the hydrogen tape. FSEC found improved selectivity


*Figure 1. Pigment films exposed to hydrogen.*

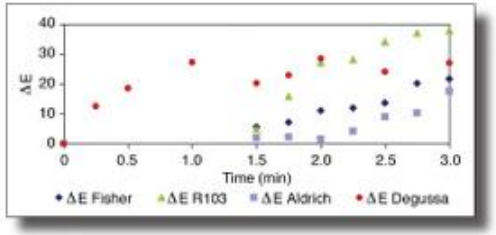



*Figure 2. Comparison of pigment formulations with exposure to hydrogen.*

Figure 3. Cross-country hydrogen lines.

Figure 4. Overhead hydrogen lines and Fixed Service Structure at KSC launch pads.

with carbon monoxide exposure. Behavior at cryogenic temperatures and other possible interferences will also be examined.

This sensor presents numerous advantages over current qualitative leak detection technology. In addition to being easy to use, the sensor does not require personnel to remain present at potentially hazardous sampling sites. The sensor can be discarded without the cost of hazardous-waste disposal. Preliminary information from the Material Test for Flight Hazards indicates that the film components have been approved for Shuttle flight (MAPTIS-II database at Marshall Space Flight Center); however, further certification will be necessary before approval is granted for use on the Shuttle.

Key accomplishment:

- Demonstrated production of nonreversible pigments and applications (2005).

Key milestone:

- Demonstrate production of reversible pigments and applications (2006).

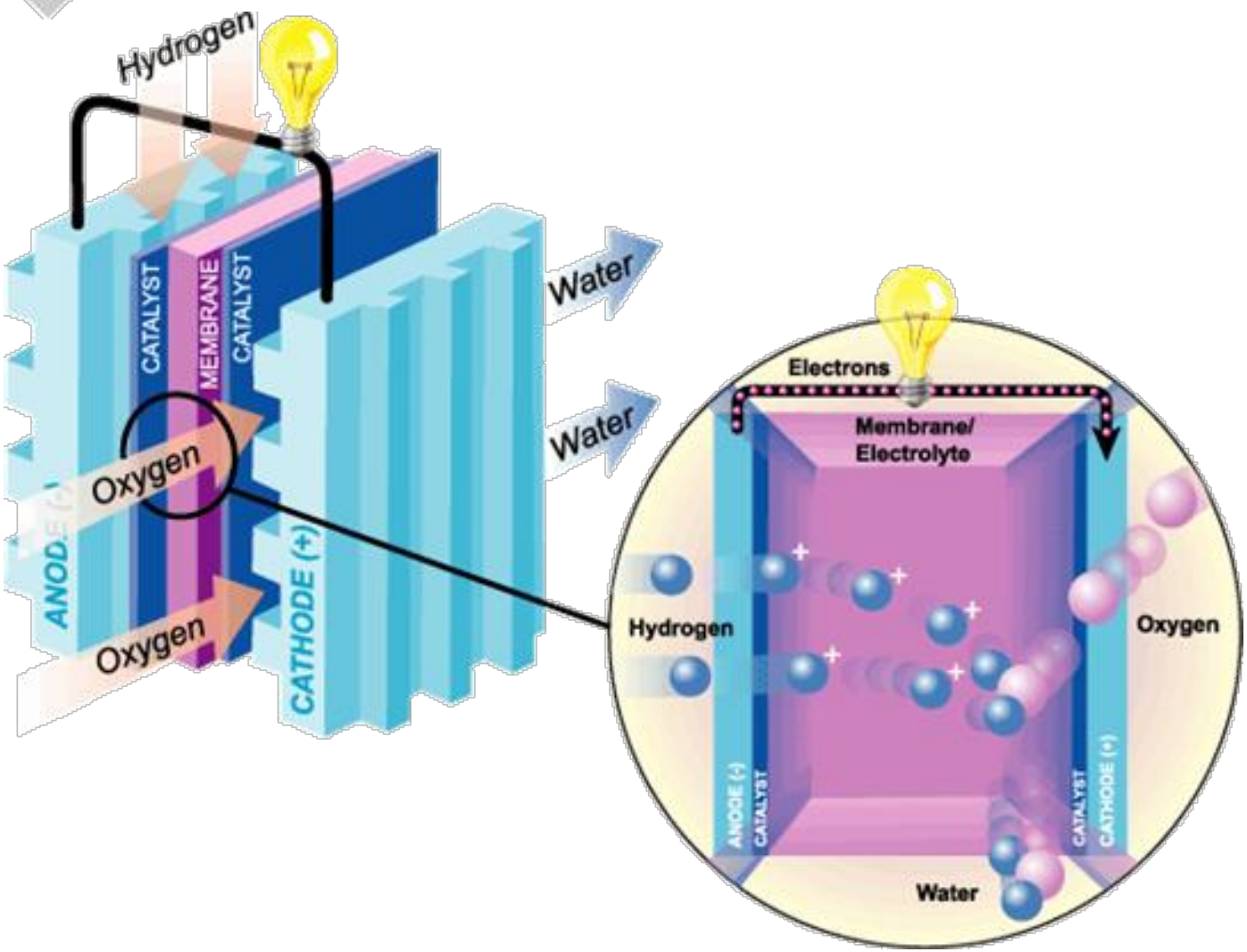
*Contact: Dr. Janine E. Captain <Janine.E.Captain@nasa.gov>, NASA KT-D2, (321) 867-6970*

*Participating Organizations: NASA KT-D1 (Dr. Robert C. Youngquist), FSEC (Dr. Gary Bokerman, Jessica H. Macpherson, Dr. Nahid Mohajeri, Dr. Nazim Muradov, and Dr. Ali T-Raissi), ASRC Aerospace (Barbara V. Peterson), NASA Space Life Sciences Training Program (Michelle M. Michalenko, Rensselaer Polytechnic Institute, New York), and University of Central Florida (Christina M. Berger and Dr. Mary C. Whitten)*

Figure 5. Checking the width of a fitting for leak-testing material on the Fixed Service Structure.

Figure 6. Michelle Michalenko places film at the Corrosion Technology Testbed for environmental exposure.

# Fuel Cell


Hydrogen
CATALYST
MEMBRANE
CATALYST
Water
Water
Oxygen
Oxygen
ANODE (-)
CATHODE (+)
Electrons
Membrane/
Electrolyte
Hydrogen
Oxygen
Water
ANODE (-)
CATALYST
CATALYST
CATHODE (+)

# *Fuel Cell (cont'd)*

- High temp PEM electrolytes - temp stability (> 125ºC), proton conductivity (> 0.1 Siemens/cm) & reduced dependence on water-saturating conditions (< 25% RH)

- High temperature, low RH polymer-type membranes (*FSEC is R&D lead for DOE's high temp, low RH membrane program*)

# *Fuel Cell (cont'd)*

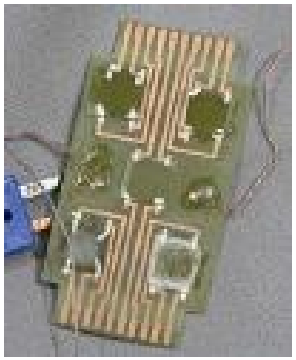
- Membrane electrode assemblies (MEA) are Nafion®-Teflon®-phosphotungstic acid based membrane & use FSEC's gas diffusion substrate (at 60$^{o}$C and under non-humidified conditions, MEA performance was close to conventional membranes in the fully hydrated state).

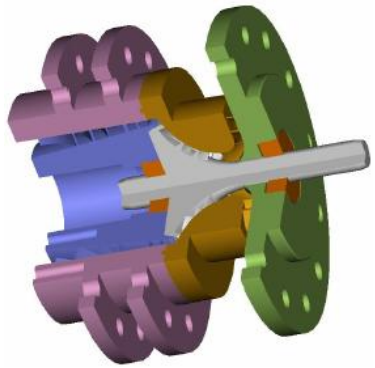
# Examples of R&D at One Consortium University

- ***University of Central Florida***
- University of Florida
- Florida State University
- University of South Florida
- Florida International University
- University of West Florida
- Florida A & M University

# UCF Projects

- Highly sensitive nano- MEMS low temperature sensor
- Wireless passive sensors & systems
- Genetic engineering of E-coli to enhance biological hydrogen production
- Shape memory actuator materials
- Hydrogen and helium separation, recovery & purification
- Reverse turbo Brayton cycle cryocooler.





# *Thank You*

## Questions??

*Hydrogen Research Database at:*

*www.fsec.ucf.edu*

*NASA-Funded Program Publications on:*

*www.hydrogenresearch.org*